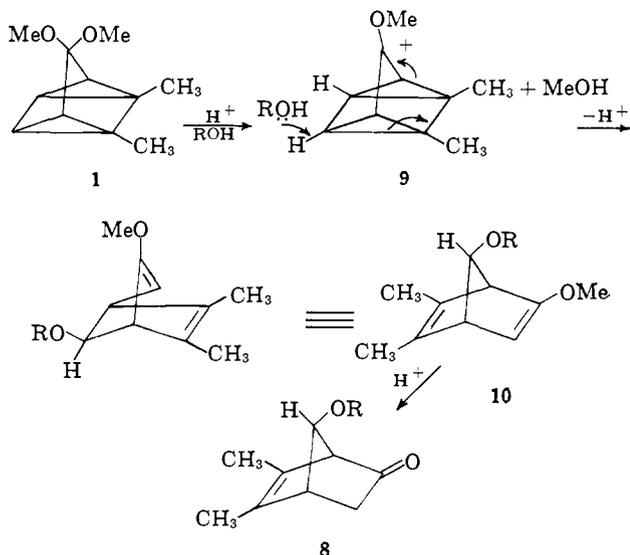


τ 6.67 (singlet), two protons at τ 8.82 (doublet), and two protons as a doublet at τ 8.51. The doublet at τ 8.51 was assigned to the hydrogens α to the ketal function and the doublet at τ 8.82 was attributed to the remaining two cyclopropyl hydrogens. The near-infrared spectrum, $\lambda_{\text{max}}^{\text{CCl}_4}$ 1.667 μ (ϵ 1.587), and the ultraviolet spectrum, end absorption 210 $m\mu$ (ϵ 380), were also consistent with the postulated structure.

Attempts to hydrolyze **1** to 2,3-dimethylquadracyclanone (**7**) led to an unexpected and intriguing result. Under the conditions of acid catalysis **1** was converted to the keto ether **8**. This conversion most likely occurs through a complex rearrangement of the initially formed carbonium ion **9**, as shown below. The manner in which **9** rearranges sheds considerable light on the fate



of a carbonium ion in the 7-position on the quadracyclane skeleton. The theoretical implications of this rearrangement in relation to nonclassical carbonium ion theory will be discussed in a future publication.

The structure of **8** was established on the basis of combined spectral and chemical evidence. The appearance of a carbonyl band at 5.72 μ coupled with the facile formation of a 2,4-dinitrophenylhydrazone confirmed the presence of a ketone function. The position of this ketone function relative to the rest of the molecule was obvious after measurement of the rearrangement product's ultraviolet spectrum (see Table I). The anomalous $n \rightarrow \pi^*$ absorption at 299 $m\mu$ (ϵ 487)

TABLE I

Structure	$\lambda_{\text{max}}^{\text{iso-octane}}$		$\lambda_{\text{max}}^{\text{c-hexane}}$	
	μ	ϵ	μ	ϵ
11	296.5	242	294	436
8	307.5	277	304	413
	319.5	177	316	242

could only be reconciled with the dehydronorcamphor skeleton,¹⁴ **11**. Since the absence of norbornenyl vinyl hydrogens was evident from both nuclear magnetic resonance and near-infrared spectroscopy, the vinylic positions must have been substituted. The presence of the methyl hydrogens at τ 8.33 and 8.41 in the nuclear magnetic resonance spectrum confirmed the placement of the methyl groups in the vinylic positions. The pres-

(14) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

ence of the methoxy group was obvious from the sharp singlet at τ 6.80 and from the infrared spectrum. Although the n.m.r. spectrum of **8** was extremely complex it was consistent with the methoxy in the 7-position being *anti* to the double bond. This was obvious from the complex nature (six broad peaks spread over 8 c.p.s.) of the single hydrogen at C-7 which appeared at τ 6.22. As was recently shown¹⁵ this requires that the C-7 proton be *syn* to the olefinic linkage with coupling to the bridgehead hydrogens and to the *endo*-hydrogen at C-6. Since there are no olefinic hydrogens, any C-7 proton *anti* to the double bond would only be split by the bridgehead hydrogens and hence would possess a simplified splitting pattern.

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(15) P. Laszlo and P. von Ragué Schleyer, *ibid.*, **86**, 1171 (1964); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(16) (a) The Ohio State University Undergraduate Research Scholar, 1962–1963; (b) The Ohio State University Undergraduate Research Scholar, 1963–1964; National Science Foundation Undergraduate Research Participant, Summer, 1963.

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The Photochemistry of 4,5-Diphenyl-2-pyrone. A Mechanistic Study

Sir:

In a recent publication¹ we reported that the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (I) gave, depending on the conditions of the irradiation, a number of products. Brief irradiation of I afforded in almost quantitative yield a compound which had been identified as 4,5-diphenyl-2-pyrone (II).¹ We now wish to present evidence which assigns structures to the remaining products and to report on the unusual photochemistry of 4,5-diphenyl-2-pyrone.

Photolysis of I in anhydrous ether at 25° with ultraviolet light of wave length above 260 $m\mu$ ² afforded a mixture of products. Consideration of the product distribution obtained in a number of photolyses *vs.* time showed an initial buildup of 4,5-diphenyl-2-pyrone (II) followed by a decrease in the amount present. Evidence that 4,5-diphenyl-2-pyrone (II) is an intermediate in the formation of the remaining products was confirmed by the finding that the photolysis of II itself in anhydrous ether afforded III, IV, and V in about the same distribution as found in runs beginning with 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (Table I).

TABLE I
PHOTOLYSIS OF 4,5-DIPHENYL-2-PYRONE (II)

Run	Time, hr.	Products, % yield			
		II	III	IV	V
1	0.16	96	0	0	0
2	1	52	24	0	0
3	2	38	19	10	6
4	4	10	14	25	17

(1) A. Padwa, *Tetrahedron Letters*, No. **15**, 813 (1964).

(2) The initial photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a corex filter to eliminate wave lengths below 260 $m\mu$.